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Effect of Temperature and Flow Rate on the Yield of Multi-walled Carbon Nanotubes by Spray Pyrolysis using *Cymbopogen flexuous* Oil

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Abstract

Carbon nanotubes (CNT) were synthesized by Chemical vapor Deposition on Fe:Mo catalyst supported on silica by using *Cymbopogen flexuous oil* and N_2 as a carrier gas. The reaction conditions are important factors that influence the yield and quality of carbon nanotubes. Different types of carbon nanostructures were obtained from spray pyrolysis of *Cymbopogen flexuous oil* at different temperature ranges from 550°C to750°C with flow rate at 20 ml per hour of carbon source. The optimum condition for synthesis of CNTs on Fe:Mo catalyst supported on silica has been reported at the temperature of 650°C and the flow rate of 20 ml per hour.

KEYWORDS: Spray pyrolysis; Carbon nanotubes; Catalysts and Temperature.

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1. INTRODUCTION

After the discovery of carbon nanotubes in 1991 (Iijima 1991) this new structure material has received a great deal of attention because of its unique applications and remarkable physical properties (Thess et al. 1996) in various fields of materials research (Iijima & Ichihashi 1993). Due to its many unique properties, the synthesis of CNTs has become a significant subject of global research.

However, the discovery of carbon nanotubes (CNTs) via the carbon –arc method with low yield and a high graphitic content made the production cost very high. For a large scale synthesis of CNTs, the decomposition of carbon containing material in the presence of catalyst seems to be more suitable (Li et al. 2004). Nowadays the Catalytic Chemical Vapor Deposition (CCVD) method appears to be a promising technique since it has the potential for a large scale synthesis of high quality single walled carbon nanotubes (SWCNTs) at relatively low cost (Liu and Fang et al 2006).

In the CCVD process, Carbon containing molecules, such as methane (Ouyang et al. 2008; Finnie et al. 2006), acetylene (Shajahan et al. 2003; Escobar et al. 2007), carbondioxide (Xu and Huang 2007), alcohol (Tian et al. 2008; Izak et al. 2007) and other hydrocarbons are used as carbon feed stock. Most of the carbon nanotubes have been synthesized from precursors based on the fossil fuel like petroleum products (Karthikeyan et al. 2009). Apart from expensiveness, these precursors are destined get depleted one day. It is therefore necessary that we look for precursors which are plant based, renewable environmentally safe. One such a natural hydrocarbon product is Cymbopogen flexuous oil. CNT's can be prepared by using this oil and Fe:Mo used as a catalyst and silica used as a supporting material at various temperature and various flow rate. Mo is widely used as a co- catalyst in metal-supported catalysts since it is known that the small amount of Mo is useful for high yield growth of CNTs. Also another major role of Mo is its usefulness for stabilization of metal nanoparticles (Ago et al. 2006).

2. EXPERIMENTAL

A Bimetallic catalyst Fe/Mo (Fe: Mo: SiO_2 =1:0.1:4) supported on silica were prepared as per the following reference (Cassel et al. 1999). Appropriate quantities of metal salts (Merck) $Fe(NO_3)_3.6\ H_2O$, $(NH_4)_6\ Mo_7O_{24}.\ 4H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated and the resultant cake heated to 90 to 100°C for 3hrs, removed from the furnace and ground into fine powder. The firm powders were then calcined for 1 hrs at 450°C and then reground before

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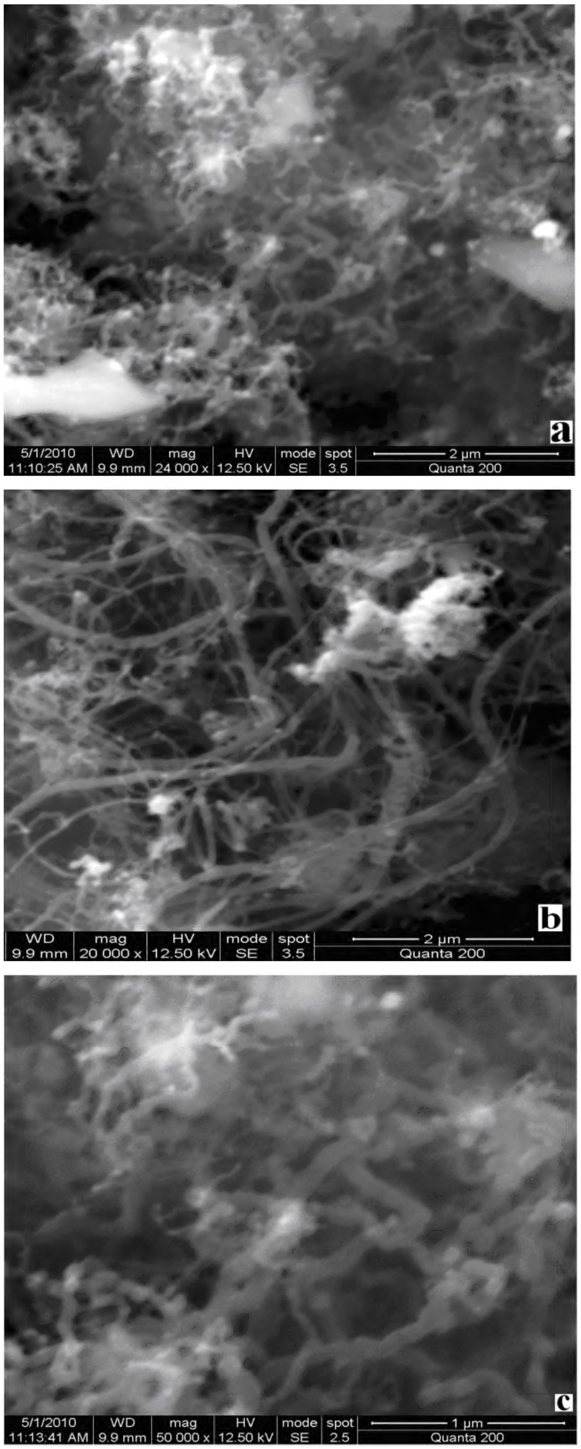

Fig. 1: SEM images of MWNTs grown on Fe,Mo catalyst supported on silica at various temperature ranging from a) 550°C, b) 650°C and c) 750°C with flow rate of 20mL per hour.

loading into the reactor. The catalyst was placed in the quartz boat that was inserted in to the center of the quartz tube placed in the heating furnace. The carrier gas Nitrogen was flushed out before switch on the reaction furnace to remove air and create nitrogen atmosphere. The temperature was raised from room temperature up to the desired growing temperature. Subsequently, *Cymbopogen flexuous oil* was introduced in to the quartz tube through spray nozzle and the flow was maintained using saline tube at the rate of 0.5 mL/min. The deposition time lasted for 30 minutes for each deposition at different temperatures from 550 to 750 °C. Nitrogen flow was maintained until the furnace yield of the Chemical vapor deposition. All the carbon mass is not getting in the form of MWNTs, the amount of amorphous carbon detected in Raman spectroscopy studies. The MWNTs were synthesized at different temperatures ranging from 550 °C to 750 °C. The amount of CNTs is directly proportional to the amount of catalyst used. The high yields of MWNTs were established as reaction temperature at 650 °C, the reaction is carried out 30 minutes.

The morphology of the sample was characterized by SEM (Hitachi S-3000H), HRTEM(JEOL-3010), XRD and Raman Spectroscopy studies was performed by JASCO NRS-1500W, the samples were prepared by sonication of products in isopropanol and few drops of resultant suspension was put on to holey carbon grid and dried.

3. RESULTS AND DISCUSSION

Cymbopogen flexuous oil is used for synthesis of Carbon nanotubes by Spry Pyrolysis method under N_2 atmosphere. This oil was sprayed over Fe/Mo catalyst supported on silica at different temperatures like 550 °C, 650 °C and 750 °C at a flow rate of 20 mL per hour were performed. As-grown carbon nanosturctures were characterized by SEM, TEM and Raman spectral studies. At 550 °C with 20 mL per hour of carbon feed stock, few multi-walled carbon nanotubes were found and we got mostly amorphous carbon with low yield. This indicates that, at lower temperature the catalyst activity is not enough for effective catalytic decomposition of *Cymbopogen flexuous* oil (Fig. 1a). An improved carbon nano structure formation at 650 ºC for the precursor flow rate of 20 ml per hour was observed with diameter around 30-40 nm with negligible amount of amorphous carbon (Fig. 1b).

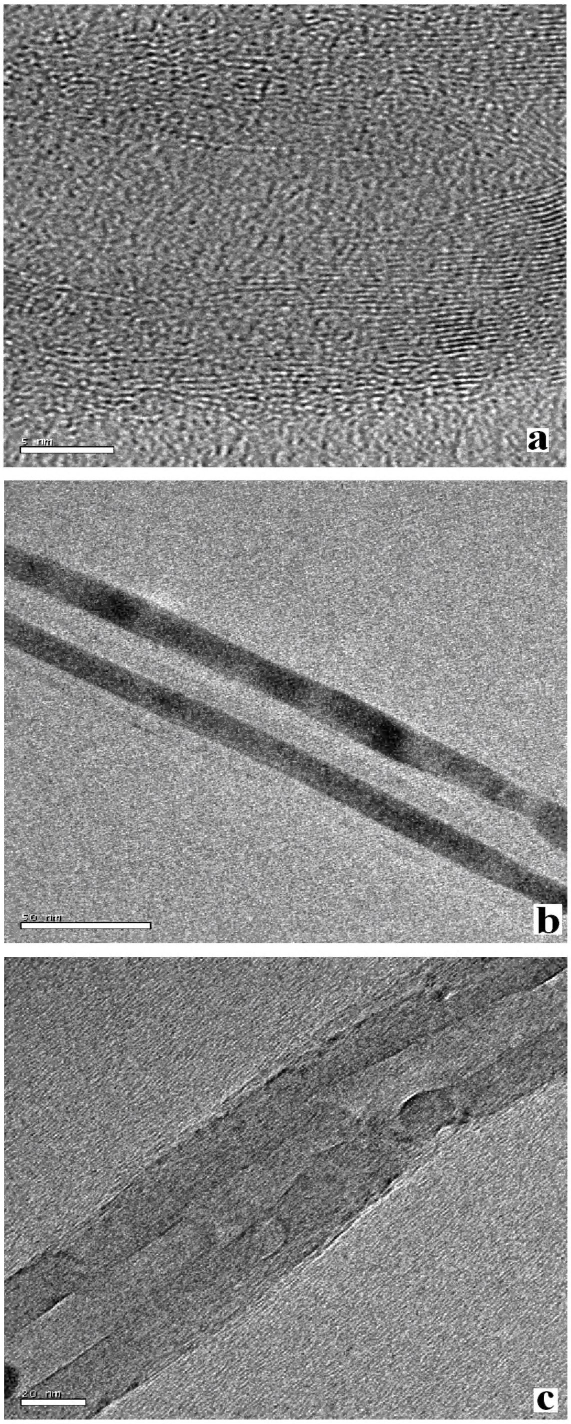

Fig. 2: TEM images of MWNTs grown on Fe,Mo catalyst supported on silica under constant temperature(650°C) at various flow rate of carbon source (a),10 mL per hour (b)20 mL per hour and (c) 30 mL per hour.

At 750 °C with carbon feed stock flow rate of 20 mL per hour , the increase in diameter of CNTs around 50-70 nm was observed (Fig.1c).

Fig.2 shows the TEM images of varied morphologies of carbon nanotubes synthesized from *cymbopogen flexuous* oil as a precursor at temperature about 650 °C with a different flow rate viz. 10 mL, 20 mL and 30 mL per hour. The Fig.2a shows TEM image of sample prepared from chosen precursor at flow rate of 20 mL per hour over silica supported Fe: Mo catalyst at a reaction temperature of 650 °C. This image indicates well graphitized layers of typical MWNTs with uniform inner and outer diameter. It also reveals that encapsulated catalyst or amorphous carbon is rarely seen in the sample.

When the precursor flow rate was increased from 10 to 20 mL per hour, due to decomposition nature of precursor and fluid nature of the catalyst particle, produced MWNTs of good quality. The TEM image also revealed that encapsulated catalyst or amorphous carbon is rarely seen in the sample. An increase of precursor flow rate to 30 mL per hour at 650 °C produced certain amount of amorphous carbon and small quantity of metal incorporated MWNTS with increase of diameter. TEM image also reveals that the tubes are not straight and continuous hollow for a long distance. The walls are frequently bridged and some defects are also seen.

An increase of precursor concentration leads to increase in decomposition of precursor over catalyst. Above the critical concentration of precursor, rate of decomposition of precursor exceeds rate of diffusion of carbon into the catalyst particle and thus encapsulation of metal particle occurs.

An addition conformation for higher degree of graphitization of as-grown MWNTs using the precursor flow rate 20 mL per hour at the reaction temperature at 650 °C is shown by raman spectra in Fig.3. The G band at around 1569 cm^{-1} is assigned to C-C vibration frequency of the carbon material with a sp^2 orbital structure and the D band at around 1360 cm^{-1} is contributed to the disorder induced vibration of C-C band (Dresselhaus et al. 2002 ; Huh et al. 2003).

The relative intensity ratio I_G/I_D of the G band and D band for the sample prepared with precursor flow rate 20 ml per hour at 650 °C indicates less defects in as grown sample (Fig. 3).

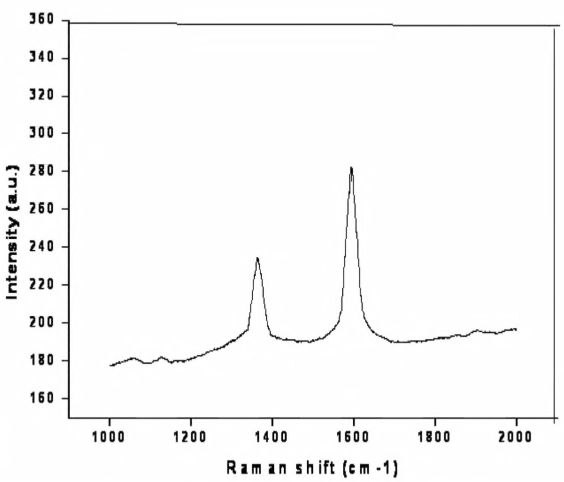

Fig.3: Typical Raman spectrum of the MWNTs grown at 650°C with the flow rate of carbon source is 20mL per hour.

4. CONCLUSION

In the synthesis of carbon nanotubes by Spry Pyrolysis method, the temperature and feed rate of carbon source plays a key role. The results show that when the flow rate of carbon source is lower than 20mL per hour, there were few CNTs formed with low yield, and when the flow rate of carbon source higher than 20mL more and more amorphous carbons were formed in the CNTs with decreasing of yield percentage. The optimum condition for synthesis of CNTs from chosen precursor is 650 °C with the flow rate of 20mL per hour.

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